

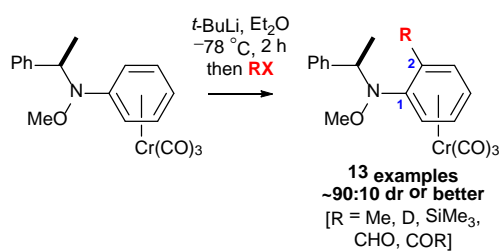
## Asymmetric *ortho*-deprotonation of ( $\eta^6$ -arene) chromium tricarbonyl complexes substituted with a chiral hydroxylamine

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## Abstract

The use of *O*-methyl-*N*-( $\alpha$ -methylbenzyl)hydroxylamine as a novel chiral auxiliary in asymmetric *ortho*-deprotonation of the ( $\eta^6$ -arene) chromium tricarbonyl complexes is described. Upon quenching of the resultant *ortho*-lithiated complex with an electrophile, 1,2-disubstituted ( $\eta^6$ -arene) chromium tricarbonyl complexes were obtained in good yield and excellent levels of diastereoselectivity.

**Key words:** arene chromium tricarbonyl; asymmetric synthesis; diastereoselective deprotonation; hydroxylamines

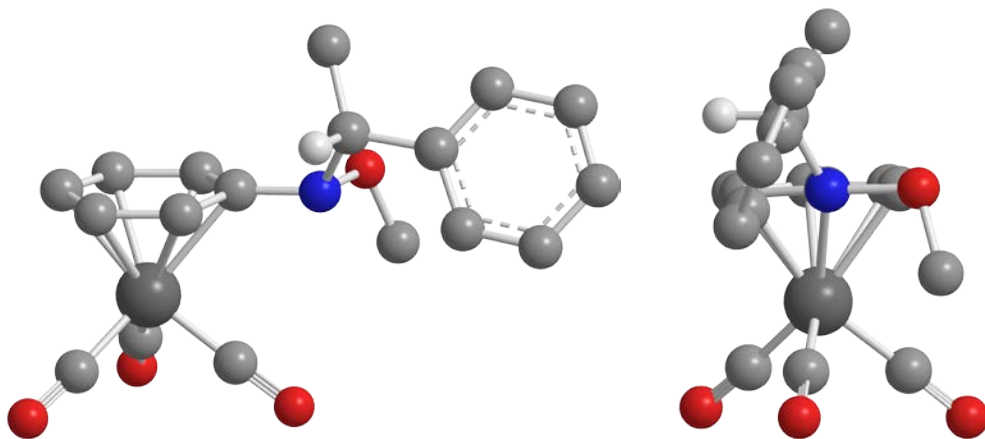
## 1. Introduction

The organic chemistry of ( $\eta^6$ -arene) chromium tricarbonyl complexes has been the subject of much interest due to their unique chemical and stereochemical properties.<sup>1,2,3</sup> ( $\eta^6$ -Arene) chromium tricarbonyl complexes have found many applications as versatile intermediates in organic synthesis, with most organic functional groups being tolerated.<sup>1-3</sup> These complexes have also been used as catalysts for a number of synthetic transformations.<sup>4</sup> They have been used in significant applications involving stereoselective transformations and asymmetric synthesis as effective intermediates or catalysts.<sup>3,5,6</sup> Since *ortho*-unsymmetrically disubstituted arene complexes are chiral, methods to form enantiomerically pure *ortho*-disubstituted ( $\eta^6$ -arene) chromium tricarbonyl complexes by asymmetric synthesis via *ortho*-deprotonation<sup>7,8</sup> or catalysis<sup>9</sup> have been reported. Diastereoselective *ortho*-deprotonation can be achieved by attachment of a chiral auxiliary to the complexed arene ring,<sup>7</sup> and enantioselective *ortho*-deprotonation can be accomplished using

enantiomerically pure bases.<sup>8</sup> We have developed methodology for the synthesis of chiral hydroxylamine chromium tricarbonyl complexes<sup>10</sup> upon nucleophilic aromatic substitution of the anion derived from *N,O*-disubstituted hydroxylamines and ( $\eta^6$ -fluorobenzene)tricarbonylchromium(0). Herein, we describe the use of the chiral complex  $\{\eta^6$ -[*O*-methyl-*N*-( $\alpha$ -methylbenzyl)hydroxyamino]benzene}tricarbonylchromium(0), to induce regio- and diastereoselective *ortho*-deprotonation of the complexed arene.

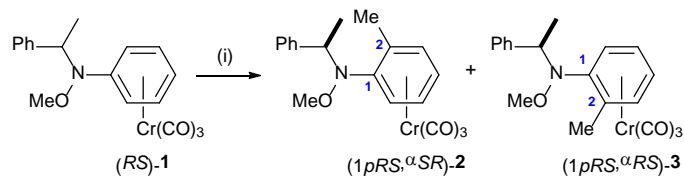
## 2. Results and discussion

The diastereoselective *ortho*-deprotonation of  $\{\eta^6$ -[(*RS*)-*O*-methyl-*N*-( $\alpha$ -methylbenzyl)hydroxyamino]benzene}tricarbonylchromium(0) (*RS*)-**1** presents an interesting mechanistic conundrum: by analogy to the regio- and diastereoselective *ortho*-lithiation of the corresponding sulfoxide  $\{\eta^6$ -[(*RS*)-phenylsulfinyl]benzene}tricarbonylchromium(0),<sup>7e</sup> where the lithium base preferentially chelates to the oxygen atom as opposed to the sulfur atom upon formation of the monoanion, the possibility of chelation to either the oxygen atom or nitrogen atom within **1** upon treatment with an alkyllithium base could potentially direct the *ortho*-lithiation with opposing diastereoselectivities. In the known solid state conformation of (*R*)-**1**,<sup>10</sup> the bulky  $\alpha$ -methylbenzyl group projects away from the chromium tricarbonyl moiety and the complexed arene ring is *anti* to the phenyl group of the  $\alpha$ -methylbenzyl fragment. Unusually for an aniline, the nitrogen atom is significantly pyramidalised (presumably to minimise steric interactions between the bulky  $\alpha$ -methylbenzyl group and the sterically demanding chromium tricarbonyl moiety) and adopts an (*S*)-configuration, which projects the nitrogen lone pair towards the *pro-S* *ortho*-proton. The N–O bond lies approximately in the same plane as the complexed arene ring and projects towards the *pro-R* *ortho*-proton (Figure 1). Assuming that the transition state for *ortho*-deprotonation of (*RS*)-**1** adopts a similar conformation in solution, the diastereoselective *ortho*-deprotonation of (*RS*)-**1** therefore represents a mechanistic probe to examine the mode of chelation in this system, with N vs. O chelation expected to give different diastereoisomeric products.



**Figure 1.** X-ray crystal structure of (*R*)-**1**<sup>10</sup> viewed perpendicular to the N–C(1) bond (*left*) and along the N–C(1) bond (*right*) [selected H atoms have been omitted for clarity, and only one of the two subtly different conformers of (*R*)-**1** present within the asymmetric unit is displayed here].

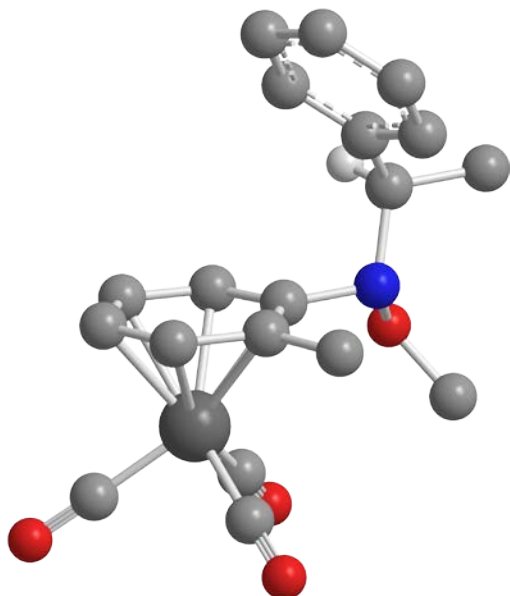
Experiments involving racemic complex (*RS*)-**1** were carried out in order to optimise procedures for diastereoselective *ortho*-deprotonation and probe the effects of chelation. Complex (*RS*)-**1**<sup>11</sup> was prepared, as previously reported,<sup>10</sup> upon nucleophilic aromatic substitution of ( $\eta^6$ -fluorobenzene)tricarbonylchromium(0) and (*RS*)-*O*-methyl-*N*-( $\alpha$ -methylbenzyl)hydroxylamine. The diastereotopic *ortho* protons within complex (*RS*)-**1** were clearly distinguishable at  $\delta_{\text{H}} = 5.25$  and 5.15 ppm in the <sup>1</sup>H NMR spectrum of (*RS*)-**1**. Treatment of (*RS*)-**1** with either *n*-BuLi or *t*-BuLi, at either  $-78$  °C or  $-100$  °C in Et<sub>2</sub>O, followed by reaction of the resultant carbanion with methyl iodide, gave mixtures of the diastereoisomeric C(2)-methyl substituted complexes (*1pRS*, $\alpha$ *SR*)-**2** and (*1pRS*, $\alpha$ *RS*)-**3**, which could be distinguished in the <sup>1</sup>H NMR spectra of the crude reaction mixtures by the resonances corresponding to the C(2)-methyl groups (i.e.,  $\delta_{\text{H}} = 2.22$  ppm for **2** and  $\delta_{\text{H}} = 2.34$  ppm for **3**). Employing *n*-BuLi gave fairly low conversion to the alkylated products **2** and **3** in relatively poor diastereoselectivity, whereas *t*-BuLi promoted superior conversion and diastereoselectivity. The use of Et<sub>2</sub>O as the solvent was preferred, since the use of THF resulted in the formation of complex mixtures of products. The optimal conditions were 1.3 equiv of *t*-BuLi at  $-78$  °C; in this case, purification by flash column chromatography followed by recrystallisation from *n*-hexane/Et<sub>2</sub>O gave the major diastereoisomer (*1pRS*, $\alpha$ *SR*)-**2** in 53% isolated yield and >99:1 dr (Scheme 1).



Base (equiv)	Temp (°C)	Conv. to 2/3 (%)	crude dr [2:3]
<i>n</i> -BuLi (1.0)	-78	0	--
<i>n</i> -BuLi (2.0)	-78	21	76:24
<i>n</i> -BuLi (10.0)	-78	26	73:27
<i>t</i> -BuLi (1.0)	-78	65	88:12
<i>t</i> -BuLi (1.3)	-78	73	91:9 <sup>a</sup>
<i>t</i> -BuLi (2.0)	-78	63	88:12
<i>t</i> -BuLi (1.3)	-100	48	91:9

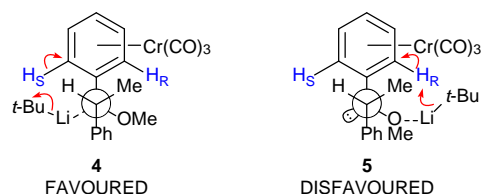
**Scheme 1.** Reagents and conditions: (i) *n*-BuLi or *t*-BuLi, Et<sub>2</sub>O, -78 °C or -100 °C, 2 h then MeI, -78 °C to rt, 16 h. [<sup>a</sup> (1*pRS*,*αSR*)-**2** was isolated in 53% yield and >99:1 dr].

The relative configuration<sup>12</sup> within (1*pRS*,*αSR*)-**2** was established by single crystal X-ray diffraction analysis.<sup>13</sup> Upon examination of this X-ray crystal structure, it can be seen that **2** adopts a conformation whereby the nitrogen atom is pyramidalised and its lone pair is approximately in the same plane as the complexed arene ring to minimise 1,3-allylic strain, with the methoxy group (as opposed to the bulky *α*-methylbenzyl fragment) projecting towards the chromium tricarbonyl moiety. The conformation with respect to rotation about the N–C(*α*) bond is staggered and the C(*α*)–H atom is placed in between the arene ring and methoxy substituent. However, the conformation with respect to rotation about the N–O bond is eclipsed, presumably to minimise the steric interactions between the methoxy group and both the *α*-methylbenzyl fragment and complexed arene ring (Figure 2). It is noteworthy that the conformation of the C(2)-methyl substituted complex **2** is different to that of the precursor **1**, where the complexed arene ring is *anti* to the phenyl group. Presumably this conformational change is required to minimise steric interactions between the chiral auxiliary and the C(2)-methyl substituent within **2**.



**Figure 2.** X-ray crystal structure of (1*pRS*, $\alpha$ *SR*)-**2** (selected H atoms have been omitted for clarity).

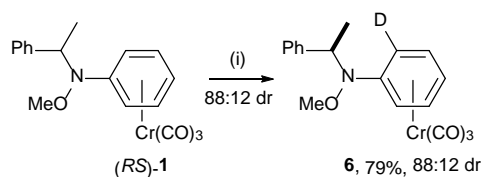
Based on this established stereochemical outcome, the origin of the regio- and diastereoselective *ortho*-deprotonation of (*RS*)-**1** can be rationalised in terms of chelation to the nitrogen atom of the *O*-methyl-*N*-( $\alpha$ -methylbenzyl)hydroxylamino chiral auxiliary. Assuming that reaction occurs via a similar conformation to that exhibited by (*R*)-**1** in the solid state<sup>10</sup> [where the bulky  $\alpha$ -methylbenzyl group projects away from the chromium tricarbonyl moiety, the complexed arene ring is *anti* to the phenyl group of the  $\alpha$ -methylbenzyl fragment, and the nitrogen atom is pyramidalised and adopts an (*S*)-configuration], the diastereoselective formation of **2** is consistent with co-ordination of lithium to the nitrogen atom, which delivers the base to the proximal *pro-S* *ortho*-proton, and deprotonation is followed by methylation of the resultant carbanion intermediate. The deprotonation of the alternative *pro-R* *ortho*-proton, via chelation to the oxygen atom, is presumably disfavoured by interactions between the C( $\alpha$ )-methyl group and the base (Figure 3).



**Figure 3.** Proposed transition state model for chelation controlled *ortho*-deprotonation; depicted for complex (*R*)-**1** as Newman projections viewed along the C( $\alpha$ )-N bond, where deprotonation of the *pro-S* *ortho*-proton ( $H_S$ ) is favoured.

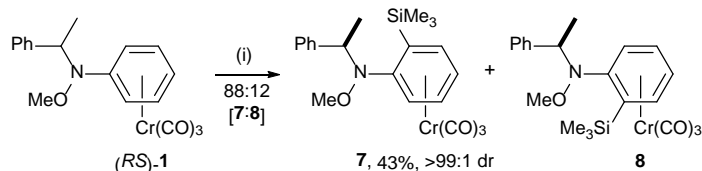
Further evidence for the high regio- and diastereoselectivity observed upon *ortho*-deprotonation of **1** was obtained from a deuteration study. *t*-BuLi (1.3 equiv) was added to a solution of (*RS*)-**1** in Et<sub>2</sub>O at  $-78$  °C, followed by the addition of MeOH-*d*<sub>4</sub>, which gave **6** in 79% yield and 88:12 dr (Scheme 2). The relative configuration within **6** was assigned by analogy to the stereochemical outcome observed upon methylation

of **1**. No evidence for the formation of a di-*ortho*-deuteriated complex was observed in the  $^1\text{H}$  NMR spectrum of the crude reaction mixture, contrary to that observed for  $(\eta^6\text{-anisole})\text{tricarbonylchromium}(0)^{14}$  and  $(\text{diphenylsulfoxide})\text{tricarbonylchromium}(0)^{7e}$ .



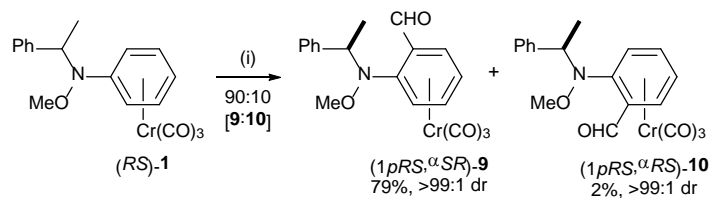
**Scheme 2.** Reagents and conditions: (i)  $t\text{-BuLi}$ ,  $\text{Et}_2\text{O}$ ,  $-78^\circ\text{C}$ , 2 h then  $\text{MeOH-}d_4$ ,  $-78^\circ\text{C}$  to rt, 16 h.

With the identification of the conditions for the highly regio- and diastereoselective *ortho*-deprotonation of **1** established, the resultant carbanion was reacted with a range of alternative electrophiles. In an analogous procedure, a solution of  $(RS)\text{-1}$  in  $\text{Et}_2\text{O}$  was sequentially reacted with  $t\text{-BuLi}$  and  $\text{TMSCl}$ . Inspection of the  $^1\text{H}$  NMR spectrum of the crude reaction mixture indicated that an 88:12 mixture of two C(2)-silyl substituted chromium tricarbonyl complexes **7** and **8**, respectively, had been produced. Purification of the crude reaction mixture via flash column chromatography gave the major diastereoisomer **7** in 43% yield and  $>99:1$  dr (Scheme 3). Again, the relative configurations within **7** and **8** were assigned by analogy to the stereochemical outcome observed upon methylation of **1**.



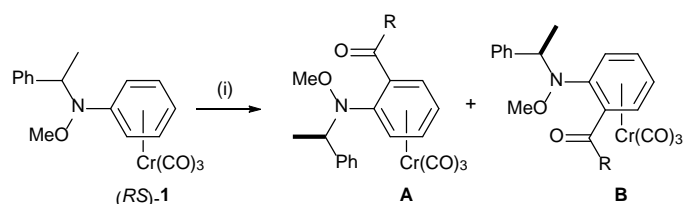
**Scheme 3.** Reagents and conditions: (i)  $t\text{-BuLi}$ ,  $\text{Et}_2\text{O}$ ,  $-78^\circ\text{C}$ , 2 h then  $\text{TMSCl}$ ,  $-78^\circ\text{C}$  to rt, 16 h.

The reaction was repeated using ethyl formate as electrophile, which gave a 90:10 mixture of the C(2)-formyl substituted complexes **9** and **10**, respectively. Purification of the crude reaction mixture by flash column chromatography and recrystallisation from  $n\text{-hexane}/\text{Et}_2\text{O}$  gave **9** and **10** as single diastereoisomers ( $>99:1$  dr) in 79 and 2% yield, respectively (Scheme 4). In this case, further evidence for the proposed structure of **9** was obtained from infra-red analysis which showed a fourth carbonyl absorption band at  $1681\text{ cm}^{-1}$  attributed to the presence of  $\text{C}=\text{O}$  stretching frequency of the formyl unit. The relative configurations within **9** and **10** were again assigned by analogy to the stereochemical outcome observed upon methylation of **1**.



**Scheme 4.** Reagents and conditions: (i) *t*-BuLi, Et<sub>2</sub>O, –78 °C, 2 h then HCO<sub>2</sub>Et, –78 °C to rt, 16 h.

Following the same methodology, a series of ketones were prepared by deprotonation of (RS)-**1** with *t*-BuLi followed by reaction of the resultant carbanion with the corresponding acyl chlorides. Upon reaction with acetyl chloride, a 91:9 mixture of **11** and **20**, respectively, was produced. Following purification of the crude reaction mixture, **11** and **20** were isolated in 82 and 9% yield, respectively, as single diastereoisomers (>99:1 dr) in each case. However, when pivaloyl chloride was used only **12** was observed in the <sup>1</sup>H NMR spectrum of the crude reaction mixture, and **12** was subsequently isolated in 99% yield and >99:1 dr. Similarly high levels of diastereoselectivity were observed upon reaction with benzoyl chloride, a range of substituted benzoyl chlorides, and 2-furoyl chloride; following purification of the crude reaction mixtures **13–19** were isolated as single diastereoisomers (>99:1 dr) in 41–82% yield (Scheme 5). In each case, the relative configurations within **11–19** were assigned by analogy to the stereochemical outcome observed upon methylation of **1**. In these latter cases, acylation of the minor diastereoisomeric carbanion intermediate is presumably disfavoured for these larger electrophiles, resulting in the exclusive formation of the (1*pRS*, $\alpha$ *SR*)-diastereoisomers **12–19**.

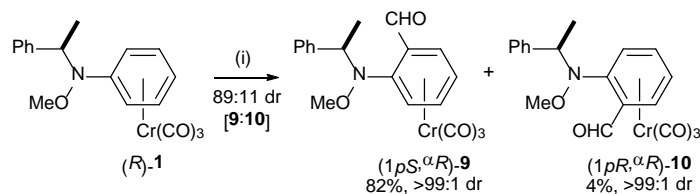


R	A	B	crude dr [A:B]	yield of A (%)	isolated dr [A:B]
Me	<b>11</b>	<b>20</b>	91:9	82 <sup>a</sup>	>99:1
<i>t</i> -Bu	<b>12</b>	<b>21</b>	>95:5	99	>99:1
Ph	<b>13</b>	<b>22</b>	>95:5	71	>99:1
2-ClC <sub>6</sub> H <sub>4</sub>	<b>14</b>	<b>23</b>	>95:5	75	>99:1
3-ClC <sub>6</sub> H <sub>4</sub>	<b>15</b>	<b>24</b>	>95:5	41	>99:1
4-ClC <sub>6</sub> H <sub>4</sub>	<b>16</b>	<b>25</b>	>95:5	60	>99:1
3-FC <sub>6</sub> H <sub>4</sub>	<b>17</b>	<b>26</b>	>95:5	60	>99:1
3-BrC <sub>6</sub> H <sub>4</sub>	<b>18</b>	<b>27</b>	>95:5	60	>99:1
2-Fur	<b>19</b>	<b>28</b>	>95:5	82	>99:1

**Scheme 5.** Reagents and conditions: (i) *t*-BuLi, Et<sub>2</sub>O, –78 °C, 2 h then RCOCl, –78 °C to rt, 16 h. [<sup>a</sup> **20** was also isolated in 9% yield and >99:1 dr; 2-Fur = furan-2-yl].

With this methodology established and optimized for the preparation of racemic complexes, it was extended to enantiomerically pure complex (*R*)-**1**, which was prepared as previously reported.<sup>10</sup> A solution of (*R*)-**1** in Et<sub>2</sub>O at –78 °C was treated with *t*-BuLi and ethyl formate to give (1*pS*, $\alpha$ *R*)-**9** and (1*pR*, $\alpha$ *R*)-**10** in 89:11 dr.

Purification of the crude reaction mixture via flash column chromatography gave (1*pS*,*αR*)-**9** and (1*pR*,*αR*)-**10** as single diastereoisomers (>99:1 dr) in 82 and 4% yield, respectively (Scheme 6). The <sup>1</sup>H and <sup>13</sup>C NMR spectroscopic data for (1*pS*,*αR*)-**9** and (1*pR*,*αR*)-**10** were entirely consistent with those for the corresponding racemic samples (1*pRS*,*αSR*)-**9** and (1*pRS*,*αRS*)-**10**.



**Scheme 6.** Reagents and conditions: (i) *t*-BuLi, Et<sub>2</sub>O, -78 °C, 2 h then HCO<sub>2</sub>Et, -78 °C to rt, 16 h.

### 3. Conclusion

In conclusion, the highly regio- and diastereoselective synthesis of 1,2-disubstituted ( $\eta^6$ -arene) chromium tricarbonyl complexes may be achieved in good yield and excellent diastereoselectivity upon diastereoselective *ortho*-deprotonation of { $\eta^6$ -[*O*-methyl-*N*-( $\alpha$ -methylbenzyl)hydroxyamino]benzene}-tricarbonylchromium(0) followed by reaction of the resultant carbanion with a range of electrophiles. Upon treatment with *t*-BuLi at -78 °C, lithium co-ordination to the nitrogen lone pair of the *O*-methyl-*N*-( $\alpha$ -methylbenzyl)hydroxylamino chiral auxiliary effects deprotonation of the proximal *ortho*-proton. The methodology employed in the racemic series has been extended to include enantiomerically pure complexes. This procedure should be readily applicable to the preparation of a broad range of enantiomerically pure 1,2-disubstituted ( $\eta^6$ -arene) chromium tricarbonyl complexes.

## 4. Experimental

### 4.1. General Experimental

All reactions involving air sensitive reagents and organometallic complexes, as well as their purifications, were performed under an atmosphere of dry nitrogen and all solvents were degassed before use. All solvents were distilled under a nitrogen atmosphere. Et<sub>2</sub>O and THF were distilled from Na/benzophenone ketyl. Reagents were used as purchased and when necessary were purified according to standard procedures.<sup>15</sup> *n*-BuLi and *t*-BuLi were used as solutions in hexanes and titrated against diphenylacetic acid immediately before use. Flash column chromatography was performed on silica gel (Kieselgel 60, 230-400 Mesh). Melting points were determined on a Reichert Thermovar or on a Gallenkamp melting point apparatus and are uncorrected. Optical rotations were measured using a Perkin-Elmer 241 polarimeter with a thermally water-jacketed 10 cm cell. Concentrations (*c*) are given in g/100 mL and specific rotation values are given in

units of  $10^{-1} \text{ deg cm}^2\text{g}^{-1}$ . Infrared spectra were recorded using a Perkin-Elmer 172SX Fourier Transform or a Perkin-Elmer 781 instrument.  $^1\text{H}$  NMR spectra were recorded at 200 MHz on a Varian Gemini 200 or a Bruker AC 200, at 300 MHz on a General Electrical QE-300 and at 500 MHz on a Bruker AMX 500 instrument.  $^{13}\text{C}$  NMR spectra were recorded at 50 MHz on a Bruker AC 200 and at 125 MHz on a Bruker AMX 500 instrument. NMR spectra were recorded in  $\text{CDCl}_3$ , using tetramethylsilane ( $\delta_{\text{H}}$  0.00 ppm) or residual chloroform ( $\delta_{\text{H}}$  7.26 ppm;  $\delta_{\text{C}}$  77.0 ppm) as internal standards. Chemical shifts ( $\delta$ ) are reported in ppm and coupling constants ( $J$ ) in Hz. Since some hydroxylamine complexes were found to be unstable with respect to decomplexation, it was not possible to record their  $^{13}\text{C}$  NMR spectra. Mass spectra ( $m/z$ ) were recorded on a Kratos 25 RF, a VG MicromassLab ZAB 1F, a VG MassLab 20-250 or an APCI Platform spectrometer. High resolution mass spectra (HRMS) were obtained on a VG AutoSpect instrument. Elemental analyses were performed on a Carlo Erba 1106 elemental analyser.

#### 4.2. General Procedure: diastereoselective *ortho*-deprotonation and alkylation

The requisite base was added dropwise to a solution of **1** in THF or  $\text{Et}_2\text{O}$  at  $-78^\circ\text{C}$ . After stirring at  $-78^\circ\text{C}$  for 2 h, the appropriate electrophile was added. The resultant solution was then allowed to warm slowly to rt and stirred at rt for 16 h. Either MeOH (0.5 mL) or satd aq  $\text{NaHCO}_3$  (0.5 mL) was added and the reaction mixture was then concentrated in vacuo. The residue was dissolved in  $\text{Et}_2\text{O}$  and the resultant solution was filtered through a plug of  $\text{MgSO}_4$  and silica, then concentrated in vacuo.

#### 4.3. (1*pRS*, $\alpha$ *SR*)-{ $\eta^6$ -1-[*O*-Methyl-*N*-( $\alpha$ -methylbenzyl)hydroxyamino]-2-methylbenzene}tricarbonylchromium(0) **2**

A solution of (*RS*)-**1** (50 mg, 0.14 mmol) in  $\text{Et}_2\text{O}$  (10 mL) was treated with *t*-BuLi (90  $\mu\text{L}$ , 1.93 M in hexanes, 0.18 mmol) and methyl iodide (0.10 mL, 1.6 mmol) according to the *General Procedure* to give a 91:9 mixture of **2** and **3**, respectively, as a yellow oil. Purification via flash column chromatography (eluent 40–60° C petrol/ $\text{Et}_2\text{O}$ , 9:1), followed by recrystallisation (*n*-hexane/ $\text{Et}_2\text{O}$ ), gave **2** as yellow crystals (25 mg, 53%, >99:1 dr);  $\text{C}_{19}\text{H}_{19}\text{CrNO}_4$  requires: C, 60.5; H, 5.1; N, 3.7%; found: C, 60.8; H, 4.75; N, 3.4%; mp 125–126 °C (dec.);  $\nu_{\text{max}}$  (KBr) 3074, 3031 (C–H, Ar), 2990, 2960, 2934, 2806 (C–H), 1951, 1870, 1844 (C=O), 1509, 1494, 1455 (C=C);  $\delta_{\text{H}}$  (300 MHz,  $\text{CDCl}_3$ ) 1.46 (3H, d,  $J$  6.9, C( $\alpha$ )*Me*), 2.22 (3H, s, C(2)*Me*), 3.35 (3H, s, *OMe*), 4.10 (1H, q,  $J$  6.9, C( $\alpha$ )*H*), 5.01 (1H, dd,  $J$  6.0, 1.2, C(6)*H*), 5.17 (1H, app dt,  $J$  6.0, 1.2, C(4)*H*), 5.34 (1H, app dt,  $J$  6.0, 1.2, C(5)*H*), 5.84 (1H, d,  $J$  6.3, C(3)*H*), 7.30–7.41 (5H, m, *Ph*);  $\delta_{\text{C}}$  (125

MHz, CDCl<sub>3</sub>) 12.9 (C(2)*Me*), 18.4 (C( $\alpha$ )*Me*), 61.9 (*OMe*), 66.2 (C( $\alpha$ )), 87.0, 87.6, 91.2, 94.3 (C(3), C(4), C(5), C(6)), 107.2 (C(2)), 125.2 (C(1)), 127.8, 128.2, 128.4 (*o,m,p-Ph*), 140.3 (*i-Ph*), 233.4 (Cr(CO)<sub>3</sub>); *m/z* (EI<sup>+</sup>) 377 ([M]<sup>+</sup>, 5%), 347 ([M-CH<sub>2</sub>O]<sup>+</sup>, 14), 293 ([M-3(CO)]<sup>+</sup>, 6), 263 ([M-C<sub>4</sub>H<sub>2</sub>O<sub>4</sub>]<sup>+</sup>, 41), 211 ([M-C<sub>4</sub>H<sub>2</sub>CrO<sub>4</sub>]<sup>+</sup>, 48), 196 ([M-C<sub>5</sub>H<sub>5</sub>CrO<sub>4</sub>]<sup>+</sup>, 71), 105 ([PhCHCH<sub>3</sub>]<sup>+</sup>, 100).

Data for (1*pRS*, $\alpha$ *RS*)-**3**:  $\delta_{\text{H}}$  (200 MHz, CDCl<sub>3</sub>) 1.59 (3H, d, *J* 6.9, C( $\alpha$ )*Me*), 2.34 (3H, s, C(2)*Me*), 3.63 (3H, s, *OMe*), 4.00 (1H, q, *J* 6.9, C( $\alpha$ )*H*), 4.89 (1H, app t, *J* 6.3, *Ar*), 5.06 (1H, d, *J* 6.5, *Ar*), 5.20 (1H, d, *J* 6.5, *Ar*), 5.32 (1H, app t, *J* 6.3, *Ar*), 7.30–7.42 (5H, m, *Ph*).

#### 4.3.1. Crystal Structure Determination for (1*pRS*, $\alpha$ *SR*)-{ $\eta^6$ -1-[*O*-methyl-*N*-( $\alpha$ -methylbenzyl)hydroxyamino]-2-methylbenzene}tricarbonylchromium(0) **2**

Data were collected using an Enraf-Nonius DIP2000 diffractometer with graphite monochromated Mo/K $\alpha$  radiation ( $\lambda = 0.71069$  Å) using standard procedures at 150 K. The structure was solved via direct methods (SIR93);<sup>16</sup> all non-hydrogen atoms were refined within anisotropic thermal parameters. Hydrogen atoms were added at idealized positions. The structure was refined using CRYSTALS.<sup>17</sup>

X-ray crystal structure data for (1*pRS*, $\alpha$ *SR*)-**2** [C<sub>19</sub>H<sub>19</sub>O<sub>4</sub>NCr]: *M* = 377.36, monoclinic, space group *P* 2<sub>1</sub>/*n*, *a* = 12.346(2) Å, *b* = 8.267(8) Å, *c* = 18.348(5) Å,  $\beta$  = 108.011(9)°, *V* = 1780.91(1) Å<sup>3</sup>, *Z* = 4,  $\mu$  = 0.65 cm<sup>-1</sup>, yellow block, crystal dimensions 0.31 × 0.22 × 0.22 mm. A total of 2948 unique reflections were measured for 0 <  $\theta$  < 26 and 2483 reflections were used in the refinement. The final parameters were *wR*<sub>2</sub> = 0.055 and *R*<sub>1</sub> = 0.044 [*I* > 3 $\sigma$ (*I*)].

Crystallographic data (excluding structure factors) for (1*pRS*, $\alpha$ *SR*)-**2** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 1556468. Copies of these data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif)

#### 4.4. (1*pRS*, $\alpha$ *SR*)-{ $\eta^6$ -1-[*O*-Methyl-*N*-( $\alpha$ -methylbenzyl)hydroxyamino]-2-deuteriobenzene}tricarbonylchromium(0) **6**

A solution of (*RS*)-**1** (50 mg, 0.14 mmol) in Et<sub>2</sub>O (10 mL) was treated with *t*-BuLi (90  $\mu$ L, 1.93 M in hexanes, 0.18 mmol) and MeOH-*d*<sub>4</sub> (0.2 mL, 0.41 mmol), according to the *General Procedure*, to give **6** (39 mg, 79%, 88:12 dr); C<sub>18</sub>H<sub>16</sub>DCrNO<sub>4</sub> requires C, 59.3; H, 5.0; N, 3.8%; found: C, 59.8; H, 4.6; N, 4.1%; mp 95–96 °C (dec.);  $\nu_{\text{max}}$  (KBr) 3106 (C–H, *Ar*), 2976, 2938, 2817 (C–H), 1973, 1887, 1843 (C=O), 1518, 1430

(C=C);  $\delta_{\text{H}}$  (200 MHz,  $\text{CDCl}_3$ ) 1.60 (3H, d,  $J$  6.8, C( $\alpha$ )Me), 3.62 (3H, s, OMe), 4.51 (1H, q,  $J$  6.8, C( $\alpha$ )H), 4.99 (1H, app t,  $J$  6.1, C(4)H), 5.17 (1H, d,  $J$  7.0, C(6)H), 5.38 (2H, app t,  $J$  5.1, C(3)H, C(5)H), 7.34 (5H, m, Ph);  $\delta_{\text{D}}$  (38.4 MHz,  $\text{CDCl}_3$ ) 5.28 (1D, br, C(2)D);  $m/z$  ( $\text{EI}^+$ ) 364 ( $[\text{M}]^+$ , 11%), 334 ( $[\text{M}-\text{CH}_2\text{O}]^+$ , 15), 280 ( $[\text{M}-3(\text{CO})]^+$ , 20), 250 ( $[\text{M}-\text{C}_4\text{H}_2\text{O}_4]^+$ , 43), 198 ( $[\text{M}-\text{C}_4\text{H}_2\text{CrO}_4]^+$ , 33), 183 ( $[\text{M}-\text{C}_5\text{H}_5\text{CrO}_4]^+$ , 71), 105 ( $[\text{PhCHCH}_3]^+$ , 100).

#### 4.5. (1*pRS*, $\alpha$ *SR*)-{ $\eta^6$ -1-[*O*-Methyl-*N*-( $\alpha$ -methylbenzyl)hydroxyamino]-2-(trimethylsilyl)benzene}tricarbonylchromium(0) **7**

A solution of (*RS*)-**1** (52 mg, 0.14 mmol) in  $\text{Et}_2\text{O}$  (10 mL) was treated with *t*-BuLi (0.10 mL, 1.94 M in hexanes, 0.19 mmol) and TMSCl (0.15 mL, 1.18 mmol), according to the *General Procedure*, to afford an 88:12 mixture of **7** and **8**, respectively, as a yellow oil. Purification via flash column chromatography (eluent 40–60 °C petrol/ $\text{Et}_2\text{O}$ , 19:1), followed by recrystallisation (40–60 °C petrol/ $\text{Et}_2\text{O}$ ) gave **7** as yellow crystals (27 mg, 43%, >99:1 dr);  $\text{C}_{21}\text{H}_{25}\text{CrNO}_4\text{Si}$  requires C, 57.9; H, 5.8; N, 3.2%; found: C, 58.0; H, 5.8; N, 3.2%; mp 107 °C (dec.);  $\nu_{\text{max}}$  (KBr) 3065, 3037 (C–H, Ar), 2983, 2936, 2902, 2812 (C–H), 1958, 1877 ( $\text{C}\equiv\text{O}$ ), 1509, 1453 (C=C);  $\delta_{\text{H}}$  (300 MHz,  $\text{CDCl}_3$ ) 0.46 (9H, s,  $\text{SiMe}_3$ ), 1.34 (3H, d,  $J$  6.6, C( $\alpha$ )Me), 3.31 (3H, s, OMe), 4.28 (1H, q,  $J$  6.6, C( $\alpha$ )H), 5.17 (1H, app t,  $J$  6.0, Ar), 5.35 (1H, dd,  $J$  6.0, 0.9, Ar), 5.60 (1H, dt,  $J$  6.3, 0.9, Ar), 5.65 (1H, d,  $J$  7.5, Ar), 7.29–7.40 (3H, m, Ph), 7.50 (2H, dd,  $J$  7.5, 1.5, Ph);  $\delta_{\text{C}}$  (125 MHz,  $\text{CDCl}_3$ )<sup>18</sup> 1.0 ( $\text{SiMe}_3$ ), 12.7 (C( $\alpha$ )Me), 61.6 (OMe), 67.7 (C( $\alpha$ )), 83.4, 91.6, 92.5, 98.6 (C(3), C(4), C(5), C(6)), 127.7, 128.3, 128.4 (*o,m,p*-Ph), 233.3 ( $\text{Cr}(\text{CO})_3$ );  $m/z$  ( $\text{EI}^+$ ) 435 ( $[\text{M}]^+$ , 2%), 405 ( $[\text{M}-\text{CH}_2\text{O}]^+$ , 6), 351 ( $[\text{M}-3(\text{CO})]^+$ , 5), 321 ( $[\text{M}-\text{C}_4\text{H}_2\text{O}_4]^+$ , 55), 269 ( $[\text{M}-\text{C}_4\text{H}_2\text{CrO}_4]^+$ , 47), 238 ( $[\text{M}-\text{C}_5\text{H}_5\text{CrO}_4]^+$ , 86), 105 ( $[\text{PhCHCH}_3]^+$ , 100).

#### 4.6. (1*pRS*, $\alpha$ *SR*)- and (1*pRS*, $\alpha$ *RS*)-{ $\eta^6$ -1-[*O*-Methyl-*N*-( $\alpha$ -methylbenzyl)hydroxyamino]-2-formylbenzene}tricarbonylchromium(0) (1*pRS*, $\alpha$ *SR*)-**9** and (1*pRS*, $\alpha$ *RS*)-**10**

A solution of (*RS*)-**1** (209 mg, 0.58 mmol) in  $\text{Et}_2\text{O}$  (40 mL) was treated with *t*-BuLi (0.42 mL, 1.56 M in hexanes, 0.75 mmol) and ethyl formate (0.14 mL, 1.8 mmol), according to the *General Procedure*, to give a 90:10 mixture of **9** and **10**, respectively, as a red oil. Purification via flash column chromatography (eluent 40–60 °C petrol/ $\text{Et}_2\text{O}$ , 9:1) followed by recrystallisation (*n*-hexane/ $\text{Et}_2\text{O}$ ) gave **9** as dark red crystals (178 mg, 79%, >99:1 dr) and **10** as red crystals (4 mg, 2%, >99:1 dr).

Data for (1*pRS*, $\alpha$ *SR*)-**9**: C<sub>19</sub>H<sub>17</sub>CrNO<sub>5</sub> requires C, 58.3; H, 4.4; N, 3.6%; found: C, 58.7; H, 4.4; N, 3.5%; mp 100 °C;  $\nu_{\max}$  (KBr) 3087, 3033 (C–H, Ar), 2980, 2939, 2849 (C–H), 1977, 1961, 1918, 1889 (C $\equiv$ O), 1681 (C=O), 1520, 1499, 1452, 1438 (C=C);  $\delta_{\text{H}}$  (300 MHz, CDCl<sub>3</sub>) 1.46 (3H, d, *J* 6.7, C( $\alpha$ )*Me*), 3.43 (3H, s, *OMe*), 4.23 (1H, q, *J* 6.7, C( $\alpha$ )*H*), 5.17 (1H, app t, *J* 6.3, C(4)*H*), 5.50 (1H, d, *J* 6.6, C(6)*H*), 5.75 (1H, app dt, *J* 6.6, 0.9, C(5)*H*), 5.95 (1H, dd, *J* 6.6, 0.9, C(3)*H*), 7.34 (5H, app s, *Ph*), 9.97 (1H, s, *CHO*);  $\delta_{\text{C}}$  (125 MHz, CDCl<sub>3</sub>) 13.8 (C( $\alpha$ )*Me*), 62.8 (*OMe*), 71.6 (C( $\alpha$ )), 78.8 (C(6)), 88.3 (C(4)), 90.2 (C(3)), 92.6 (C(2)), 93.3 (C(5)), 128.4, 128.5 (*o,m,p-Ph*), 134.4 (C(1)), 139.0 (*i-Ph*), 185.3 (C(2)*CHO*), 230.9 (Cr(CO)<sub>3</sub>); *m/z* (EI<sup>+</sup>) 391 ([M]<sup>+</sup>, 6%), 361 ([M–CH<sub>2</sub>O]<sup>+</sup>, 3), 307 ([M–3(CO)]<sup>+</sup>, 3), 277 ([M–C<sub>4</sub>H<sub>2</sub>O<sub>4</sub>]<sup>+</sup>, 22), 276 ([M–C<sub>4</sub>H<sub>3</sub>O<sub>4</sub>]<sup>+</sup>, 27), 225 ([M–C<sub>4</sub>H<sub>2</sub>CrO<sub>4</sub>]<sup>+</sup>, 38), 210 ([M–C<sub>5</sub>H<sub>5</sub>CrO<sub>4</sub>]<sup>+</sup>, 58), 105 ([PhCHCH<sub>3</sub>]<sup>+</sup>, 100).

Data for (1*pRS*, $\alpha$ *RS*)-**10**: mp 106–107 °C;  $\nu_{\max}$  (KBr) 3103 (C–H, Ar), 2934 (C–H), 1974, 1961, 1895, 1884 (C $\equiv$ O), 1677 (C=O), 1519, 1494, 1454, 1433 (C=C);  $\delta_{\text{H}}$  (300 MHz, CDCl<sub>3</sub>) 1.67 (3H, d, *J* 6.9, C( $\alpha$ )*Me*), 3.80 (3H, s, *OMe*), 4.23 (1H, q, *J* 6.9, C( $\alpha$ )*H*), 5.07 (1H, d, *J* 7.2, *Ar*), 5.11 (1H, app t, *J* 6.3, *Ar*), 5.54 (1H, app dt, *J* 6.6, 1.2, *Ar*), 5.98 (1H, dd, *J* 6.3, 1.2, *Ar*), 7.04 (2H, dd, *J* 7.7, 1.8, *Ph*), 7.25 (3H, m, *Ph*), 9.85 (1H, s, *CHO*); *m/z* (EI<sup>+</sup>) 391 ([M]<sup>+</sup>, 21%), 361 ([M–CH<sub>2</sub>O]<sup>+</sup>, 2), 307 ([M–3(CO)]<sup>+</sup>, 7), 277 ([M–C<sub>4</sub>H<sub>2</sub>O<sub>4</sub>]<sup>+</sup>, 29), 276 ([M–C<sub>4</sub>H<sub>3</sub>O<sub>4</sub>]<sup>+</sup>, 57), 225 ([M–C<sub>4</sub>H<sub>2</sub>CrO<sub>4</sub>]<sup>+</sup>, 16), 210 ([M–C<sub>5</sub>H<sub>5</sub>CrO<sub>4</sub>]<sup>+</sup>, 17), 105 ([PhCHCH<sub>3</sub>]<sup>+</sup>, 61), 52 ([Cr]<sup>+</sup>, 100); HRMS (EI<sup>+</sup>) C<sub>19</sub>H<sub>17</sub>CrNO<sub>5</sub><sup>+</sup> ([M]<sup>+</sup>) requires 391.0506; found 391.0480.

#### 4.7. (1*pRS*, $\alpha$ *SR*)- and (1*pRS*, $\alpha$ *RS*)-{ $\eta^6$ -1-[*O*-Methyl-*N*-( $\alpha$ -methylbenzyl)hydroxyamino]-2-acetylbenzene}tricarbonylchromium(0) **11** and **20**

A solution of (*RS*)-**1** (201 mg, 0.55 mmol) in Et<sub>2</sub>O (40 mL) was treated with *t*-BuLi (0.43 mL, 1.66 M in hexanes, 0.72 mmol) and acetyl chloride (0.12 mL, 1.7 mmol), according to the *General Procedure*, to give a 91:9 mixture of **11** and **20**, respectively, as an orange solid. Purification via flash column chromatography (eluent 40–60 °C petrol/Et<sub>2</sub>O, 19:1), followed by recrystallisation (*n*-hexane/Et<sub>2</sub>O) gave **11** (184 mg, 82%, >99:1 dr) and **20** (20 mg, 9%, >99:1 dr) as orange crystals.

Data for (1*pRS*, $\alpha$ *SR*)-**11**: C<sub>20</sub>H<sub>19</sub>CrNO<sub>5</sub> requires C, 59.3; H, 4.7; N, 3.5%; found: C, 59.6; H, 4.75; N, 3.2%; mp 91 °C;  $\nu_{\max}$  (KBr) 3062, 3033, 3000 (C–H, Ar), 2983, 2937, 2890, 2811 (C–H), 1958, 1888, 1871 (C $\equiv$ O), 1694 (C=O), 1602, 1523, 1495, 1452, 1430 (C=C);  $\delta_{\text{H}}$  (300 MHz, CDCl<sub>3</sub>) 1.39 (3H, d, *J* 6.9, C( $\alpha$ )*Me*), 2.70 (3H, s, *COMe*), 3.48 (3H, s, *OMe*), 4.12 (1H, q, *J* 6.9, C( $\alpha$ )*H*), 5.11 (1H, app t, *J* 6.3, *Ar*), 5.52 (1H, d, *J* 6.9, *Ar*), 5.63–5.67 (2H, m, *Ar*), 7.28–7.36 (5H, m, *Ph*);  $\delta_{\text{C}}$  (75 MHz, CDCl<sub>3</sub>)<sup>19</sup> 14.0 (C( $\alpha$ )*Me*), 30.4 (*COMe*), 62.5 (*OMe*), 70.2 (C( $\alpha$ )), 79.5, 88.0, 92.6, 93.2 (C(3), C(4), C(5), C(6)), 128.2, 128.4 (*o,m,p-Ph*),

139.2 (*i*-Ph), 197.9 (COMe), 231.7 (Cr(CO)<sub>3</sub>); *m/z* (EI<sup>+</sup>) 405 ([M]<sup>+</sup>, 2%), 375 ([M-CH<sub>2</sub>O]<sup>+</sup>, 2), 321 ([M-3(CO)]<sup>+</sup>, 3), 291 ([M-C<sub>4</sub>H<sub>2</sub>O<sub>4</sub>]<sup>+</sup>, 12), 290 ([M-C<sub>4</sub>H<sub>3</sub>O<sub>4</sub>]<sup>+</sup>, 14), 239 ([M-C<sub>4</sub>H<sub>2</sub>CrO<sub>4</sub>]<sup>+</sup>, 40), 224 ([M-C<sub>5</sub>H<sub>5</sub>CrO<sub>4</sub>]<sup>+</sup>, 100), 105 ([PhCHCH<sub>3</sub>]<sup>+</sup>, 81).

Data for (1*pRS*,*αRS*)-**20**: C<sub>20</sub>H<sub>19</sub>CrNO<sub>5</sub> requires C, 59.3; H, 4.7; N, 3.5%; found: C, 59.5; H, 4.5; N, 3.25%; mp 101–102 °C; *v*<sub>max</sub> (KBr) 3087, 3030 (C–H, Ar), 2965, 2927, 2851 (C–H), 1969, 1892 (C≡O), 1681 (C=O), 1605, 1517, 1494, 1455 (C=C); *δ*<sub>H</sub> (500 MHz, CDCl<sub>3</sub>) 1.69 (3H, d, *J* 7.0, C(*α*)Me), 2.83 (3H, s, COMe), 3.84 (3H, s, OMe), 3.99 (1H, q, *J* 7.0, C(*α*)H), 5.00–5.05 (2H, m, Ar), 5.38 (1H, app dt, *J* 6.5, 1.3, Ar), 5.75 (1H, dd, *J* 6.5, 1.3, Ar), 7.01 (2H, dd, *J* 8.2, 1.0, Ph), 7.18–7.27 (3H, m, Ph); *m/z* (EI<sup>+</sup>) 405 ([M]<sup>+</sup>, 1%), 375 ([M-CH<sub>2</sub>O]<sup>+</sup>, 1), 291 ([M-C<sub>4</sub>H<sub>2</sub>O<sub>4</sub>]<sup>+</sup>, 3), 239 ([M-C<sub>4</sub>H<sub>2</sub>CrO<sub>4</sub>]<sup>+</sup>, 9), 224 ([M-C<sub>5</sub>H<sub>5</sub>CrO<sub>4</sub>]<sup>+</sup>, 32), 105 ([PhCHCH<sub>3</sub>]<sup>+</sup>, 100).

#### 4.8. (1*pRS*,*αSR*)-{*η*<sup>6</sup>-1-[*O*-Methyl-*N*-(*α*-methylbenzyl)hydroxyamino]-2-pivaloylbenzene}tricarbonylchromium(0) **12**

A solution of (*RS*)-**1** (208 mg, 0.572 mmol) in Et<sub>2</sub>O (40 mL) was treated with *t*-BuLi (0.48 mL, 1.56 M in hexanes, 0.74 mmol) and pivaloyl chloride (0.35 mL, 2.84 mmol), according to the *General Procedure*, to afford an orange oil. Purification via recrystallisation (*n*-hexane/Et<sub>2</sub>O) gave **12** as orange crystals (253 mg, 99%, >99:1 dr); C<sub>23</sub>H<sub>25</sub>CrNO<sub>5</sub> requires C, 61.7; H, 5.6; N, 3.1%; found: C, 61.9; H, 5.6; N, 3.0%; mp 80 °C (dec.); *v*<sub>max</sub> (KBr) 3096, 3064 (C–H, Ar), 2975, 2935, 2870, 2818 (C–H), 1957, 1867 (C≡O), 1695 (C=O), 1583, 1521, 1496, 1479, 1450 (C=C); *δ*<sub>H</sub> (300 MHz, CDCl<sub>3</sub>) 0.86 (9H, s, CMe<sub>3</sub>), 1.70 (3H, d, *J* 6.9, C(*α*)Me), 3.51 (3H, s, OMe), 4.75 (2H, m, C(*α*)H, Ar), 5.08 (1H, d, *J* 6.6, Ar), 5.24 (1H, dd, *J* 6.3, 1.2, Ar), 5.49 (1H, app dt, *J* 6.3, 1.2, Ar), 7.25–7.36 (5H, s, Ph); *δ*<sub>C</sub> (125 MHz, CDCl<sub>3</sub>) 17.6 (C(*α*)Me), 27.9 (CMe<sub>3</sub>), 44.2 (CMe<sub>3</sub>), 62.2 (OMe), 65.2 (C(*α*)), 76.5, 83.1, 91.4, 93.4 (C(3), C(4), C(5), C(6)), 102.1 (C(2)), 128.1, 128.3, 128.5 (*o,m,p*-Ph), 130.4 (C(1)), 139.0 (*i*-Ph), 204.9 (C(2)CO), 232.8 (Cr(CO)<sub>3</sub>); *m/z* (ESI<sup>+</sup>) 448 ([M+H]<sup>+</sup>, 100%).

#### 4.9. (1*pRS*,*αSR*)-{*η*<sup>6</sup>-1-[*O*-Methyl-*N*-(*α*-methylbenzyl)hydroxyamino]-2-benzoylbenzene}tricarbonylchromium(0) **13**

A solution of (*RS*)-**1** (658 mg, 1.81 mmol) in Et<sub>2</sub>O (80 mL) was treated with *t*-BuLi (1.42 mL, 1.66 M in hexanes, 2.36 mmol) and benzoyl chloride (0.63 mL, 5.4 mmol), according to the *General Procedure*, to afford an orange oil. Purification via flash column chromatography (eluent 40–60 °C petrol/Et<sub>2</sub>O, 9:1),

followed by recrystallisation (*n*-hexane/Et<sub>2</sub>O) gave **13** as orange crystals (601 mg, 71%, >99:1 dr); C<sub>25</sub>H<sub>21</sub>CrNO<sub>5</sub> requires C, 64.2; H, 4.5; N, 3.0%; found: C, 64.5; H, 4.4; N, 2.7%; mp 97 °C (dec.);  $\nu_{\max}$  (KBr) 3079, 3028 (C–H, Ar), 2979, 2933, 2813 (C–H), 1960, 1893, 1867 (C≡O), 1675 (C=O), 1598, 1581, 1520, 1492, 1449 (C=C);  $\delta_{\text{H}}$  (300 MHz, CDCl<sub>3</sub>) 1.49 (3H, d, *J* 6.6, C( $\alpha$ )Me), 3.42 (3H, s, OMe), 4.46 (1H, br q, C( $\alpha$ )H), 4.92 (1H, app t, *J* 6.0, Ar), 5.33–5.37 (2H, m, Ar), 5.56 (1H, app t, *J* 6.3, Ar), 7.12–7.32 (7H, m, Ph), 7.50 (3H, m, Ph); *m/z* (ESI<sup>+</sup>) 468 ([M+H]<sup>+</sup>, 100%).

#### 4.10. (1*pRS*, $\alpha$ *SR*)-{ $\eta^6$ -1-[*O*-Methyl-*N*-( $\alpha$ -methylbenzyl)hydroxyamino]-2-(2'-chlorobenzoyl)benzene}tricarbonylchromium(0) **14**

A solution of (*RS*)-**1** (201 mg, 0.553 mmol) in Et<sub>2</sub>O (40 mL) was treated with *t*-BuLi (0.43 mL, 1.66 M in hexanes, 0.72 mmol) and 2-chlorobenzoyl chloride (0.18 mL, 1.38 mmol), according to the *General Procedure*, to afford an orange oil. Purification via flash column chromatography (eluent 40–60 °C petrol/Et<sub>2</sub>O, 9:1), followed by recrystallisation (*n*-hexane/Et<sub>2</sub>O) gave **14** as orange crystals (209 mg, 75%, >99:1 dr); C<sub>25</sub>H<sub>20</sub>ClCrNO<sub>5</sub> requires C, 59.8; H, 4.0; N, 2.8%; found: C, 59.6; H, 4.0; N, 2.5%; mp 136 °C (dec.);  $\nu_{\max}$  (KBr) 3065, 3032 (C–H, Ar), 2975, 2937 (C–H), 1972, 1904, 1885 (C≡O), 1672 (C=O), 1591, 1559, 1541, 1515, 1498, 1458, 1450, 1434 (C=C);  $\delta_{\text{H}}$  (300 MHz, CDCl<sub>3</sub>) 1.36 (3H, d, *J* 6.9, C( $\alpha$ )Me), 3.28 (3H, s, OMe), 4.81 (1H, q, *J* 6.9, C( $\alpha$ )H), 4.88 (1H, app dt, *J* 6.2, 0.9, Ar), 5.48 (1H, d, *J* 6.9, Ar), 5.73 (1H, d, *J* 6.6, Ar), 5.84 (1H, app t, *J* 6.3, Ar), 7.29–7.48 (6H, m, Ar, Ph), 7.57–7.60 (1H, m, Ar, Ph), 7.76 (2H, d, *J* 7.5, Ar, Ph); *m/z* (ESI<sup>+</sup>) 504 ([M(<sup>37</sup>Cl)+H]<sup>+</sup>, 30%), 502 ([M(<sup>35</sup>Cl)+H]<sup>+</sup>, 100%).

#### 4.11. (1*pRS*, $\alpha$ *SR*)-{ $\eta^6$ -1-[*O*-Methyl-*N*-( $\alpha$ -methylbenzyl)hydroxyamino]-2-(3'-chlorobenzoyl)benzene}tricarbonylchromium(0) **15**

A solution of (*RS*)-**1** (201 mg, 0.553 mmol) in Et<sub>2</sub>O (40 mL) was treated with *t*-BuLi (0.43 mL, 1.66 M in hexanes, 0.72 mmol) and 3-chlorobenzoyl chloride (0.20 mL, 1.56 mmol), according to the *General Procedure*, to afford an orange oil. Purification via flash column chromatography (eluent 40–60 °C petrol/Et<sub>2</sub>O, 9:1), followed by recrystallisation (*n*-hexane/Et<sub>2</sub>O) gave **15** as orange crystals (114 mg, 41%, >99:1 dr); C<sub>25</sub>H<sub>20</sub>ClCrNO<sub>5</sub> requires C, 59.8; H, 4.0; N, 2.8%; found: C, 59.7; H, 4.0; N, 2.6%; mp 110 °C (dec.);  $\nu_{\max}$  (KBr) 3087, 3065, 3029 (C–H, Ar), 2992, 2946, 2817 (C–H), 1973, 1890, 1873 (C≡O), 1674 (C=O), 1593, 1573, 1518, 1493, 1470, 1450 (C=C);  $\delta_{\text{H}}$  (300 MHz, CDCl<sub>3</sub>) 1.52 (3H, d, *J* 6.9, C( $\alpha$ )Me), 3.46 (3H, s, OMe), 4.50 (1H, br q, C( $\alpha$ )H), 4.92 (1H, app t, *J* 6.0, Ar), 5.28–5.32 (2H, m, Ar), 5.57 (1H, app dt, *J*

6.2, 0.9, Ar), 7.08–7.25 (7H, m, Ar, Ph), 7.45 (1H, d, *J* 7.2, Ar, Ph), 7.62 (1H, s, Ar); *m/z* (ESI<sup>+</sup>) 504 ([M(<sup>37</sup>Cl)+H]<sup>+</sup>, 30%), 502 ([M(<sup>35</sup>Cl)+H]<sup>+</sup>, 100%).

**4.12. (1*pRS*,*αSR*)-{ $\eta^6$ -1-[*O*-Methyl-*N*-(*α*-methylbenzyl)hydroxyamino]-2-(4'-chlorobenzoyl)benzene}tricarbonylchromium(0) **16****

A solution of (*RS*)-**1** (202 mg, 0.556 mmol) in Et<sub>2</sub>O (40 mL) was treated with *t*-BuLi (0.44 mL, 1.66 M in hexanes, 0.72 mmol) and 4-chlorobenzoyl chloride (0.20 mL, 1.67 mmol), according to the *General Procedure*, to afford an orange oil. Purification via flash column chromatography (eluent 40–60 °C petrol/Et<sub>2</sub>O, 9:1), followed by recrystallisation (*n*-hexane/Et<sub>2</sub>O) gave **16** as orange crystals (167 mg, 60%, >99:1 dr); C<sub>25</sub>H<sub>20</sub>ClCrNO<sub>5</sub> requires C, 59.8; H, 4.0; N, 2.8%; found: C, 59.8; H, 4.0; N, 2.6%; mp 112 °C (dec.);  $\nu_{\max}$  (KBr) 3089, 3031 (C–H, Ar), 2980, 2941, 2817 (C–H), 1963, 1908, 1883 (C≡O), 1677 (C=O), 1588, 1575, 1519, 1495, 1451 (C=C);  $\delta_{\text{H}}$  (300 MHz, CDCl<sub>3</sub>) 1.54 (3H, d, *J* 6.9, C( $\alpha$ )*Me*), 3.47 (3H, s, *OMe*), 4.53 (1H, br q, C( $\alpha$ )*H*), 4.91 (1H, app t, *J* 6.0, Ar), 5.31 (2H, d, *J* 6.3, Ar), 5.59 (1H, app dt, *J* 6.5, 0.9, Ar), 7.06–7.37 (9H, m, Ar, Ph); *m/z* (ESI<sup>+</sup>) 504 ([M(<sup>37</sup>Cl)+H]<sup>+</sup>, 30%), 502 ([M(<sup>35</sup>Cl)+H]<sup>+</sup>, 100%).

**4.13. (1*pRS*,*αSR*)-{ $\eta^6$ -1-[*O*-Methyl-*N*-(*α*-methylbenzyl)hydroxyamino]-2-(3'-fluorobenzoyl)benzene}tricarbonylchromium(0) **17****

A solution of (*RS*)-**1** (224 mg, 0.617 mmol) in Et<sub>2</sub>O (40 mL) was treated with *t*-BuLi (0.48 mL, 1.66 M in hexanes, 0.80 mmol) and 3-fluorobenzoyl chloride (0.23 mL, 1.89 mmol), according to the *General Procedure*, to afford an orange oil. Purification via flash column chromatography (eluent 40–60 °C petrol/Et<sub>2</sub>O, 9:1), followed by recrystallisation (*n*-hexane/Et<sub>2</sub>O), gave **17** as orange crystals (180 mg, 60%, >99:1 dr); C<sub>25</sub>H<sub>20</sub>CrFNO<sub>5</sub> requires C, 61.9; H, 4.15; N, 2.9%; found: C, 61.7; H, 3.9; N, 2.9%; mp 80 °C (dec.);  $\nu_{\max}$  (KBr) 3085 (C–H, Ar), 2982, 2935 (C–H), 1964, 1886 (C≡O), 1681 (C=O), 1589, 1520, 1495, 1484, 1446 (C=C);  $\delta_{\text{H}}$  (300 MHz, CDCl<sub>3</sub>) 1.53 (3H, d, *J* 6.9, C( $\alpha$ )*Me*), 3.47 (3H, s, *OMe*), 4.51 (1H, br q, C( $\alpha$ )*H*), 4.90 (1H, app t, *J* 6.0, Ar), 5.28–5.31 (2H, m, Ar), 5.57 (1H, app t, *J* 6.0, Ar), 7.09–7.24 (9H, m, Ar, Ph); *m/z* (ESI<sup>+</sup>) 486 ([M+H]<sup>+</sup>, 100%).

**4.14. (1*pRS*,*αSR*)-{ $\eta^6$ -1-[*O*-Methyl-*N*-(*α*-methylbenzyl)hydroxyamino]-2-(3'-bromobenzoyl)benzene}tricarbonylchromium(0) **18****

A solution of (*RS*)-**1** (238 mg, 0.656 mmol) in Et<sub>2</sub>O (40 mL) was treated with *t*-BuLi (0.51 mL, 1.66 M in hexanes, 0.85 mmol) and 3-bromobenzoyl chloride (0.26 mL, 1.97 mmol), according to the *General Procedure*, to afford an orange oil. Purification via flash column chromatography (eluent 40–60 °C petrol/Et<sub>2</sub>O, 9:1), followed by recrystallisation (*n*-hexane/Et<sub>2</sub>O), gave **18** as orange crystals (215 mg, 60%, >99:1 dr); C<sub>25</sub>H<sub>20</sub>BrCrNO<sub>5</sub> requires C, 55.0; H, 3.7; N, 2.6%; found: C, 55.25; H, 3.6; N, 2.35%; mp 80 °C (dec.);  $\nu_{\max}$  (KBr) 3086, 3063, 3028 (C–H, Ar), 2990, 2945, 2816 (C–H), 1973, 1888, 1872 (C≡O), 1673 (C=O), 1590, 1568, 1517, 1493, 1467, 1450 (C=C);  $\delta_{\text{H}}$  (300 MHz, CDCl<sub>3</sub>) 1.52 (3H, d, *J* 6.6, C( $\alpha$ )*Me*), 3.46 (3H, s, *OMe*), 4.47 (1H, br q, C( $\alpha$ )*H*), 4.92 (1H, app t, *J* 5.7, Ar), 5.30–5.32 (2H, m, Ar), 5.57 (1H, app t, *J* 6.0, Ar), 7.09–7.25 (7H, m, Ar, *Ph*), 7.60 (1H, d, *J* 7.8, Ar), 7.84 (1H, d, *J* 0.9, Ar); *m/z* (ESI<sup>+</sup>) 548 ([M(<sup>81</sup>Br) + H]<sup>+</sup>, 95%), 546 ([M(<sup>79</sup>Br) + H]<sup>+</sup>, 100%).

**4.15. (1*pRS*,*αSR*)-{ $\eta^6$ -1-[*O*-Methyl-*N*-(*α*-methylbenzyl)hydroxyamino]-2-(furan-2'-carbonyl)benzene}tricarbonylchromium(0) **19****

A solution of (*RS*)-**1** (650 mg, 1.79 mmol) in Et<sub>2</sub>O (80 mL) was treated with *t*-BuLi (1.4 mL, 1.66 M in hexanes, 2.33 mmol) and 2-furoyl chloride (0.53 mL, 5.37 mmol), according to the *General Procedure*, to afford an orange oil. Purification via flash column chromatography (eluent 40–60 °C petrol/Et<sub>2</sub>O, 9:1), followed by recrystallisation (*n*-hexane/Et<sub>2</sub>O) gave **19** as orange crystals (669 mg, 82%, >99:1 dr); C<sub>23</sub>H<sub>19</sub>CrNO<sub>6</sub> requires C, 60.4; H, 4.2; N, 3.1%; found: C, 60.4; H, 4.4; N, 3.0%; mp 85 °C (dec.);  $\nu_{\max}$  (KBr) 3094, 3031 (C–H, Ar), 2976, 2934, 2814 (C–H), 1963, 1957, 1869 (C≡O), 1669 (C=O), 1570, 1523, 1499, 1467, 1453 (C=C);  $\delta_{\text{H}}$  (300 MHz, CDCl<sub>3</sub>) 1.44 (3H, d, *J* 6.6, C( $\alpha$ )*Me*), 3.37 (3H, s, *OMe*), 4.35 (1H, br q, C( $\alpha$ )*H*), 5.01 (1H, app t, *J* 6.0, Ar), 5.40 (1H, d, *J* 6.3, Ar), 5.51 (1H, d, *J* 6.0, Ar), 5.58 (1H, app t, *J* 6.0, Ar), 6.48 (1H, s, C(4')*H*), 7.11–7.28 (6H, m, C(3')*H*, *Ph*), 7.57 (1H, s, C(5')*H*); *m/z* (ESI<sup>+</sup>) 458 ([M+H]<sup>+</sup>, 100%).

**4.16. (1*pS*,*αR*)- and (1*pR*,*αR*)-{ $\eta^6$ -1-[*O*-Methyl-*N*-(*α*-methylbenzyl)hydroxyamino]-2-formylbenzene}tricarbonylchromium(0) (1*pS*,*αR*)-**9** and (1*pR*,*αR*)-**10****

A solution of complex (*R*)-**1** (100 mg, 0.28 mmol) in Et<sub>2</sub>O (20 mL) was treated with *t*-BuLi (0.23 mL, 1.56 M in hexanes, 0.36 mmol) and ethyl formate (0.10 mL, 1.2 mmol), according to the *General Procedure*, to

give an 89:11 mixture of **9** and **10**, respectively, as a red oil. Purification via flash column chromatography (eluent 40–60 °C petrol/Et<sub>2</sub>O, 9:1) followed by recrystallisation (*n*-hexane/Et<sub>2</sub>O) gave (1*pS*,*αR*)-**9** as dark red crystals (89 mg, 82%, >99:1 dr) and (1*pR*,*αR*)-**10** as red crystals (4 mg, 4%, >99:1 dr).

Data for (1*pS*,*αR*)-**9**: mp 100 °C;  $[\alpha]_D^{23}$  –860.3 (*c* 0.3 in CHCl<sub>3</sub>).

Data for (1*pR*,*αR*)-**10**: mp 104–105 °C;  $[\alpha]_D^{23}$  +926.1 (*c* 0.1 in CHCl<sub>3</sub>).

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